



# Oxidation of gaseous elemental mercury by hydrochloric acid over $\text{CuCl}_2/\text{TiO}_2$ -based catalysts in SCR process

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## ABSTRACT

$\text{CuCl}_2/\text{TiO}_2$ -based catalysts were examined to investigate the role of copper chloride for the oxidation of gaseous elemental mercury in selective catalytic reduction (SCR) process.  $\text{CuCl}_2$  on  $\text{CuCl}_2/\text{TiO}_2$  catalyst was decomposed releasing Cl by calcination at high temperatures and restored to its original form by being exposed to gas phase HCl, reversibly. The activity for mercury oxidation was significantly increased with the increase of  $\text{CuCl}_2$  loading and HCl concentration.  $\text{CuCl}_2/\text{TiO}_2$  catalysts revealed high activity for mercury oxidation even in the absence of HCl. This suggests that mercury oxidation could occur via a Mars–Maessen mechanism by which adsorbed or weakly bound  $\text{Hg}^0$  would react with Cl in  $\text{CuCl}_2$  that is replenished from gas phase HCl. However, the activity of  $\text{CuCl}_2$ -loaded catalysts for NO removal considerably decreased with the increase of temperature above 300–350 °C, which may be due to the ability of  $\text{CuCl}_2$  for  $\text{NH}_3$  oxidation in SCR reaction.

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## 1. Introduction

Among the various air pollutants emitted from coal-fired power plant, atmospheric emission of elemental mercury is becoming a major environmental issue that attracts considerable attention in recent years, since mercury is a volatile and persistent pollutant that accumulates in the food chain and has neurological health effect [1,2]. The coal-fired power plant has been known to be the largest anthropogenic source of mercury emissions, accounting for approximately half to one-third of mercury emissions in the world [3,4]. Therefore, a variety of technologies have been studied to develop efficient and cost-effective technologies to remove mercury from coal-fired power plant, such as conventional air pollution control devices [5,6], sorbent injection [7–11], electro-catalytic oxidation [12], photochemical oxidation [13–17], oxidizing agents injection and catalytic oxidation [18–21].

Mercury exists in three forms in coal-fired flue gas: elemental ( $\text{Hg}^0$ ), oxidized ( $\text{Hg}^{2+}$ ), and particle-bound ( $\text{Hg}(\text{p})$ ). Among the mercury species,  $\text{Hg}^{2+}$  and  $\text{Hg}(\text{p})$  are relatively easy to remove from flue gas by using typical air pollution control devices (APCDs) such as ESPs (Electrostatic Precipitators) and wet-FGD (Flue Gas Desulfurization). Elemental mercury ( $\text{Hg}^0$ ), however, is difficult to capture,

since it is insoluble in water. Among the technologies being considered for mercury reduction in coal-fired power plant is thus the combination of a catalyst and a wet scrubber; the catalyst oxidizes  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  and the oxidized mercury is subsequently absorbed by the scrubber system [22]. Catalysts capable of significant conversion of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  would have tremendous value because the oxidized mercury can be removed concurrently with acid gases during FGD process. In the coal-derived flue gases, chlorine is believed to be mainly present in the form of HCl. It indicates that HCl is a most important species affecting mercury oxidation, since the major oxidized mercury species in coal-derived flue gas is  $\text{HgCl}_2$  [23]. Therefore, the effect of HCl on the oxidation of  $\text{Hg}^0$  to oxidized Hg such as  $\text{HgCl}_2$  has been most widely studied in the area of mercury removal technologies [24–26].

Selective catalytic reduction (SCR) has been a widely commercialized technology for controlling emissions of  $\text{NO}_x$  from power plant [27–29]. In addition to  $\text{NO}_x$  control SCR catalyst has been found to affect the mercury speciation by altering  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  in the presence of HCl. Several mechanisms have been proposed for catalytic mercury oxidation by HCl over SCR catalyst ( $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ ). Niksa and Fujiwara [30,31] proposed that mercury oxidation occurs via an Eley–Rideal mechanism where adsorbed HCl reacts with gas phase or weakly adsorbed  $\text{Hg}^0$ . An Eley–Rideal reaction between adsorbed  $\text{Hg}^0$  and gas phase HCl was proposed by Senior [32]. On the other hand, other researchers proposed that mercury oxidation could occur between adsorbed  $\text{Hg}^0$  and HCl adsorbed at an adjacent site via a Langmuir–Hinshelwood

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**Table 1**

Physicochemical properties of catalysts employed in this study.

Catalysts	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Content (wt%)		
			CuCl <sub>2</sub> <sup>a</sup>	V <sub>2</sub> O <sub>5</sub>	WO <sub>3</sub>
CuCl <sub>2</sub> (1.5)/TiO <sub>2</sub>	83.4	0.282	1.51	–	–
CuCl <sub>2</sub> (3)/TiO <sub>2</sub>	80.7	0.259	3.07	–	–
CuCl <sub>2</sub> (6)/TiO <sub>2</sub>	75.2	0.261	5.47	–	–
CuCl <sub>2</sub> (3)-V <sub>2</sub> O <sub>5</sub> (2)/TiO <sub>2</sub>	65.6	0.198	3.22	2.04	–
V <sub>2</sub> O <sub>5</sub> (2)/TiO <sub>2</sub>	70.6	0.321	–	2.01	–
Commercial SCR catalyst	79.4	0.278	–	1.68	7.60

<sup>a</sup> wt% as of copper.

mechanism [33,34]. There is still controversy on reaction mechanisms for mercury oxidation. However, consistent observations have been reported for the effect of NH<sub>3</sub> inhibiting the mercury oxidation by HCl, regardless of proposed mechanisms. When NH<sub>3</sub> is present in the reactant gas stream with HCl, the extent of mercury oxidation decreases with the increase of NH<sub>3</sub>/NO ratio (higher NH<sub>3</sub> concentration) [30–36]. This is attributed to that NH<sub>3</sub> preferentially adsorb and inhibit the adsorption of HCl promoting Hg<sup>0</sup> oxidation on the catalyst surface in SCR process. Note that NH<sub>3</sub> present in the reactant gas stream has been well known to easily and strongly adsorb on the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-based SCR catalyst surface [37,38]. Therefore, in order to obtain sufficient activity for Hg<sup>0</sup> oxidation by overcoming such inhibiting effect of NH<sub>3</sub> in SCR process, the oxidation of Hg<sup>0</sup> by HCl should proceed via a mechanism which is different from the proposed mechanisms such as Eley–Rideal and Langmuir–Hinshelwood mechanisms. CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalyst was employed in this study, since chlorine in CuCl<sub>2</sub> could act as oxidant to promote Hg<sup>0</sup> oxidation even in the presence of NH<sub>3</sub>. The insight of the application of CuCl<sub>2</sub> catalyst to facilitate the Hg<sup>0</sup> oxidation was obtained from the widely commercialized process for the production of 1,2-dichloroethane by catalytic oxychlorination of ethylene with hydrochloric acid and oxygen [39–42]. The CuCl<sub>2</sub> catalyst supported on alumina has been commercial used for the reaction. The oxychlorination has been supposed to occur in three subsequent steps; (i) reduction of CuCl<sub>2</sub> into CuCl by ethylene, (ii) reoxidation of CuCl by oxygen, and (iii) closure of the loop by restoration of the original CuCl<sub>2</sub> with HCl. Because TiO<sub>2</sub> has been widely used as a support of V<sub>2</sub>O<sub>5</sub>-based SCR catalyst due to its high resistance to SO<sub>2</sub>, TiO<sub>2</sub> was chosen as a support material in this study.

In the present study, the performance and stability of CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalyst for the oxidation of mercury and the removal of NO<sub>x</sub> were studied to evaluate its possibility as a catalyst for simultaneous removal of mercury and NO<sub>x</sub> in SCR process. To understand the reaction mechanism involved in the catalytic oxidation of mercury over CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalyst, the activity for mercury oxidation was investigated with respect to reaction conditions such as oxidation and SCR conditions and different concentration of HCl. The activities of CuCl<sub>2</sub>/TiO<sub>2</sub> catalyst for mercury oxidation and NO<sub>x</sub> removal were also compared to those of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> commercial SCR catalyst.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

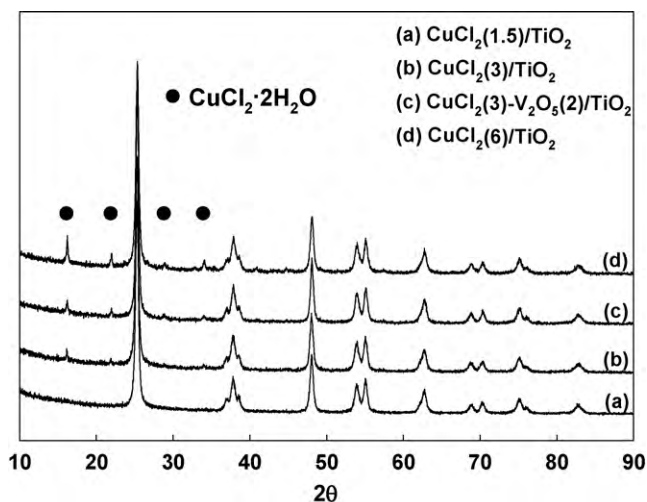
The CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalysts employed in this study were prepared by impregnation method using anatase-type TiO<sub>2</sub> (MC90, Ishihara Corp., USA) as catalyst support. A CuCl<sub>2</sub> aqueous solution prepared by dissolving CuCl<sub>2</sub>·2H<sub>2</sub>O in deionized water was impregnated into TiO<sub>2</sub> in rotary vacuum evaporator operated at 65 °C, 600 mm Hg and 60 rpm. The CuCl<sub>2</sub>-impregnated sample was then dried at 120 °C overnight. The content of CuCl<sub>2</sub> in the catalyst

was adjusted by controlling the concentration of CuCl<sub>2</sub> aqueous solution. V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was prepared by impregnating aqueous solution of NH<sub>4</sub>VO<sub>3</sub> mixed with oxalic acid into the TiO<sub>2</sub>. The molar ratio of NH<sub>4</sub>VO<sub>3</sub> to oxalic acid used for preparing the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was employed as 2. The sample was then dried at 120 °C overnight and followed by calcination under air atmosphere at 500 °C for 2 h. The CuCl<sub>2</sub>-loaded V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was also prepared by the same method as that of CuCl<sub>2</sub>/TiO<sub>2</sub> catalyst. To compare the activities of prepared CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalysts with commercial SCR catalyst for mercury oxidation and NO removal, a V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> commercial SCR catalyst for coal-fired power plant was also employed in this study, which contains 1.68 and 7.60 wt% of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub>, respectively.

The physicochemical properties of CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalysts and commercial SCR catalyst employed in this study were summarized in Table 1. The catalyst compositions were determined by a sequential X-ray fluorescence spectrometer (Rigaku, Model ZSX). The numbers in the parentheses of catalyst name are the target contents of Cu and V<sub>2</sub>O<sub>5</sub> which are intended to load when preparing the catalysts. There is no significant difference between actually loaded Cu and V<sub>2</sub>O<sub>5</sub> and their intended contents as shown in Table 1. The catalyst surface area was measured by BET method with Micromeritics ASAP 2010 apparatus using liquid N<sub>2</sub> at 77 K. The average pore diameter and pore volume were obtained from N<sub>2</sub> desorption isotherm. Powder X-ray diffraction (XRD) patterns were measured on a PANalytical X'Pert diffractometer with an X'Celerator detector. Data were collected with a fixed divergence slit (0.50°) and Soller slits (incident and diffracted = 0.04°) and Cu K<sub>α</sub> radiation. Long-step scans were taken in the 2θ range of 10–90° with a step width of 0.016° and a scanning speed of 6.5° min<sup>−1</sup> operated at 40 kV and 30 mA of X-ray gun.

### 2.2. Catalytic reactor system

The catalytic activity for mercury oxidation was examined in a fixed-bed flow reactor typically containing 1 g of 20/30 mesh size pellet. Prior to the measurement of catalytic activities for mercury oxidation and NO removal, CuCl<sub>2</sub>-loaded catalysts were pretreated in reactor system under the flow of N<sub>2</sub> at 400 and 450 °C for 2 h, respectively. A gas mixture containing 3% O<sub>2</sub> in N<sub>2</sub> balance was fed to the reactor system through mass flow controller (Brooks Model 5850E) under oxidation condition experiment. Under SCR condition experiment, NO and NH<sub>3</sub> of 500 ppm, respectively, were additionally fed to the compositions of oxidation condition. To examine the effect of HCl on the oxidation of mercury, 10–50 ppm of HCl was mixed with reactant gas stream, when added. The total reactant gas flow rate was maintained as 2 L/min. A quartz tube of inner diameter 3/8" was used as a reactor to avoid the adsorption and reaction of mercury species on the reactor surface. For the mercury oxidation experiment, the gaseous Hg<sup>0</sup> was generated by flowing N<sub>2</sub> carrier gas to a temperature-controlled impinger containing liquid mercury. The concentration of mercury could be controlled by adjusting the impinger temperature and carrier gas flow rate. The



**Fig. 1.** XRD spectra of  $\text{CuCl}_2/\text{TiO}_2$ -based catalysts with different  $\text{CuCl}_2$  loading only after drying at  $120^\circ\text{C}$  overnight.

mercury vapor in  $\text{N}_2$  carrier gas was mixed with simulated reactant gas mixture just before the catalyst bed. The  $\text{Hg}^0$  concentration in the reactant gases was maintained as about  $50\text{ }\mu\text{g}/\text{m}^3$  for all experiments.

Mercury concentration was continuously measured by cold-vapor atomic absorption spectrometer (VM-3000, Mercury Instruments Analytical Technologies) employing the resonance absorption of the mercury atoms at a wavelength of  $253.7\text{ nm}$ . The spectrometer can measure only the concentration of  $\text{Hg}^0$ . Therefore, to measure the concentration of total mercury including elemental and oxidized mercury in reactant gases, the impinger containing 10 wt% stannous chloride ( $\text{SnCl}_2$ ) solution, whose pH was about 0.5, was located at just after the reactor. The  $\text{SnCl}_2$  solution reduces all oxidized mercury species to elemental mercury. Therefore, the concentration of oxidized mercury can be measured by the difference of mercury concentration after and before passing the  $\text{SnCl}_2$  solution. To measure only  $\text{Hg}^0$  concentration, the effluent gas from the catalytic reactor was passed through the impinger containing deionized water, instead of  $\text{SnCl}_2$  solution. It took at least 1 h to obtain steady  $\text{Hg}^0$  concentration for each set of reaction conditions. The mercury oxidation efficiency can be calculated by

the following formula:

$$\text{Hg oxidation efficiency(\%)} = \frac{[\text{Hg}^{2+}]_{\text{out}}}{[\text{Hg}^0]_{\text{out}} + [\text{Hg}^{2+}]_{\text{out}}} \quad (1)$$

where,  $[\text{Hg}^0]_{\text{out}}$  and  $[\text{Hg}^{2+}]_{\text{out}}$  are the concentrations of elemental and oxidized mercury at the reactor outlet, respectively.

For the examination of catalytic activity for NO removal, the concentration of NO was analyzed by on-line chemiluminescence NO- $\text{NO}_2$  analyzer (Thermo Electron Co., Model 42C).

### 3. Results and discussion

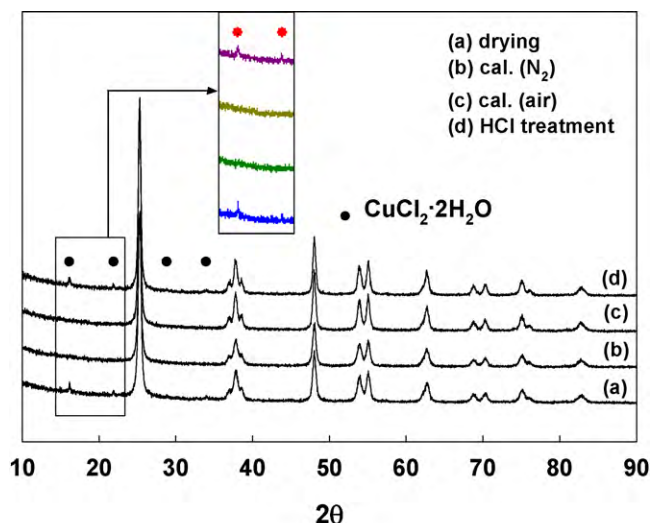
#### 3.1. Identification of $\text{CuCl}_2$ species on the catalyst

To identify the surface structure of copper species on the catalyst surface, XRD measurement was conducted for four catalysts with different copper loading or containing  $\text{V}_2\text{O}_5$  with  $\text{CuCl}_2$ . Besides peaks for  $\text{TiO}_2$  of anatase type, only peaks corresponding to hydrated  $\text{CuCl}_2$  ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) appear at  $2\theta$  value of 16.20, 21.96, 28.27 and 33.99 as shown in Fig. 1. Except the  $\text{CuCl}_2(1.5)/\text{TiO}_2$  catalyst with the lowest copper loading prepared in this study, the intensity of peaks corresponding to hydrated  $\text{CuCl}_2$  increased with the increase of copper loading. The reason for no appearance of peaks for hydrated  $\text{CuCl}_2$  on  $\text{CuCl}_2(1.5)/\text{TiO}_2$  catalyst is likely due to the small amount of  $\text{CuCl}_2$  below detection limit by XRD. The primary copper species was identified as  $\text{CuCl}_2$ , regardless of the presence of  $\text{V}_2\text{O}_5$ . No peaks for other copper compound such as  $\text{CuCl}$  were observed on all the catalysts prepared in this study. Therefore, it can be concluded that the main copper compound on the  $\text{CuCl}_2/\text{TiO}_2$ -based catalysts was  $\text{CuCl}_2$ , indicating that  $\text{CuCl}_2$  was well loaded on the catalyst surface by impregnation method employed in this study.

To investigate the stability of  $\text{CuCl}_2$  on the catalyst surface, the chemical compositions were analyzed after treating the catalysts under different atmosphere as shown in Table 2. The chemical compositions including the content of Cl adsorbed on the catalyst surface were determined by a X-ray fluorescence spectrometer. After impregnating  $\text{CuCl}_2$  to  $\text{TiO}_2$  or  $\text{V}_2\text{O}_5/\text{TiO}_2$ , the catalysts were treated by four different conditions: (i) drying at  $120^\circ\text{C}$  overnight, (ii) *in situ* calcination of the dried sample at  $400^\circ\text{C}$  under the flow of  $\text{N}_2$  for 2 h, (iii) calcination of the dried sample at  $500^\circ\text{C}$  under air atmosphere for 2 h, and (iv) exposing the sample treated by (iii) to gas flow containing HCl of 2500 ppm at  $350^\circ\text{C}$  for 8 h. The Cl content of  $\text{CuCl}_2/\text{TiO}_2$  catalysts only after drying increased with the increase of copper content of the catalyst. The molar ratios of Cl/Cu

**Table 2**  
Compositions and Cl/Cu molar ratio of  $\text{CuCl}_2/\text{TiO}_2$ -based catalysts after a variety of treatments.

Catalysts	Treatments	Compositions (wt%)			Cl/Cu
		$\text{V}_2\text{O}_5$	Cu	Cl	
$\text{CuCl}_2(1.5)/\text{TiO}_2$	Drying	–	1.51	0.89	1.05
	Calcination in $\text{N}_2$	–	1.54	0.37	0.43
	Calcination in air	–	1.63	0.02	0.02
	HCl treatment	–	1.66	1.14	1.23
$\text{CuCl}_2(3)/\text{TiO}_2$	Drying	–	3.07	2.12	1.23
	Calcination in $\text{N}_2$	–	3.28	1.01	0.55
	Calcination in air	–	3.15	0.18	0.10
	HCl treatment	–	2.90	1.13	0.70
$\text{CuCl}_2(6)/\text{TiO}_2$	Drying	–	5.47	3.60	1.18
	Calcination in $\text{N}_2$	–	4.40	1.38	0.56
	Calcination in air	–	6.53	0.89	0.24
	HCl treatment	–	5.84	3.82	1.17
$\text{CuCl}_2(3)-\text{V}_2\text{O}_5(2)/\text{TiO}_2$	Drying	2.04	3.22	1.97	1.09
	Calcination in $\text{N}_2$	1.95	3.14	0.64	0.36
	Calcination in air	2.05	3.23	0.14	0.08
	HCl treatment	1.80	3.17	1.08	0.61

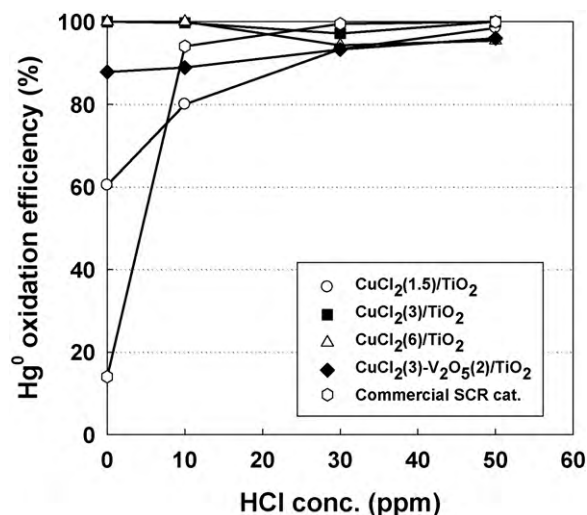


**Fig. 2.** XRD spectra of  $\text{CuCl}_2(3)/\text{TiO}_2$  catalyst after a variety of treatments; (a) drying at  $120^\circ\text{C}$  overnight, (b) *in situ* calcination of the dried sample at  $400^\circ\text{C}$  under the flow of  $\text{N}_2$  for 2 h, (c) calcination of the dried sample at  $500^\circ\text{C}$  under air atmosphere for 2 h, (d) exposing the sample treated by (c) to gas stream containing HCl 2500 ppm,  $\text{O}_2$  3% and  $\text{N}_2$  balance at  $350^\circ\text{C}$  for 8 h.

were in the range of 1.05–1.23 for all catalysts studied in this study. Since the predominant copper species existing on the catalyst surface is  $\text{CuCl}_2$  as identified by XRD, Cl/Cu molar ratios indicate that about 53–62% of copper loaded exists in the form of  $\text{CuCl}_2$ .

As shown in Table 2, the copper content was not nearly altered after calcining under the flow of  $\text{N}_2$  at  $400^\circ\text{C}$  and air atmosphere at  $500^\circ\text{C}$ . However, Cl content appreciably decreased by the two calcination treatments. The decrease of Cl content was much larger by calcination under air atmosphere than  $\text{N}_2$  flow. This may be attributed to the difference in calcination temperatures employed to two treatments. Note that the calcination under  $\text{N}_2$  flow was conducted at the temperature of  $400^\circ\text{C}$ , while that under air atmosphere at  $500^\circ\text{C}$ . Regardless of the calcination conditions, the significant decrease of Cl content may be due to the decomposition of  $\text{CuCl}_2$  on the catalyst surface. Only Cl was released from the catalyst by the decomposition of  $\text{CuCl}_2$ . Note that the change of copper content was negligible by the calcinations at high temperatures. To identify the restoration of copper species to  $\text{CuCl}_2$ , catalyst calcined under air atmosphere at  $500^\circ\text{C}$  was exposed to the gas stream containing such a high concentration of 2500 ppm HCl in 3%  $\text{O}_2$  and  $\text{N}_2$  balance at  $350^\circ\text{C}$  for 8 h. After exposed to HCl, catalysts recovered their original Cl content as shown in Table 2. This result suggests the decomposition of  $\text{CuCl}_2$  on  $\text{CuCl}_2/\text{TiO}_2$  catalyst and restoration by the presence of gas phase HCl were reversible.

XRD measurements were applied to the catalysts calcined by two different treatments. As shown in Fig. 2, the peaks for hydrated  $\text{CuCl}_2$  were disappeared by the calcinations at high temperatures. The reduction of Cl content of the  $\text{CuCl}_2/\text{TiO}_2$ -based catalyst was already observed by the calcinations at high temperatures of 400 and  $450^\circ\text{C}$ . The decrease of Cl content and the disappearance of peaks for hydrated  $\text{CuCl}_2$  identified by elemental analyses and XRD concretely supported the fact that  $\text{CuCl}_2$  on the catalyst surface decomposed releasing Cl by calcinations at high temperatures, regardless of the exposed atmosphere. However, the  $\text{CuCl}_2$  was formed again by exposing the calcined catalyst to high concentration of HCl of 2500 ppm. It was already identified that Cl content decreased by calcination under air atmosphere was recovered to its original value by exposing the catalyst to reactant gas stream containing HCl. Based on the reversible decomposition and restoration of  $\text{CuCl}_2$  on the catalyst surface, it can be postulated that steady concentration of  $\text{CuCl}_2$  can be maintained on the catalyst surface at



**Fig. 3.** Effect of HCl concentration on the oxidation of elemental mercury to oxidized mercury under oxidation condition; gas flow rate =  $2\text{ L/min}$ , reaction temperature =  $350^\circ\text{C}$ ,  $[\text{O}_2] = 3\%$ ,  $[\text{Hg}] = 50\text{ }\mu\text{g/m}^3$ ,  $[\text{HCl}] = 0\text{--}50\text{ ppm}$ ,  $[\text{N}_2]$  balance.

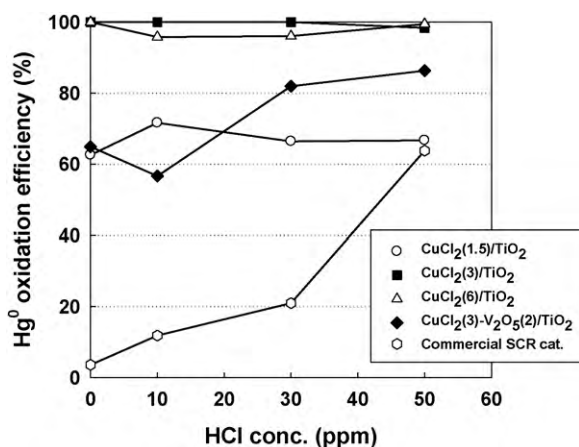
actual reaction temperature of SCR process, when gas phase HCl is present in the reactant gas stream.

### 3.2. Effect of HCl on the oxidation efficiency of $\text{Hg}^0$ under oxidation condition

Fig. 3 shows the effect of HCl on the efficiency for the oxidation of elemental mercury to oxidized mercury over a series of  $\text{CuCl}_2/\text{TiO}_2$  catalysts with different loading of  $\text{CuCl}_2$  under oxidation condition. For comparison, the oxidation efficiency of commercial  $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$  SCR catalyst was also included in Fig. 3. The activity for  $\text{Hg}^0$  oxidation was nearly negligible in the absence of HCl, while greatly increased by the addition of HCl to the reactant gas stream over commercial SCR catalyst. More than 90% conversion for mercury oxidation was observed over commercial  $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$  catalyst. It has been reported that HCl significantly promoted the oxidation of elemental mercury to oxidized mercury such as  $\text{HgCl}_2$  over a various kinds of heterogeneous catalysts [25,26,30–36]. The promoting effect of HCl on  $\text{Hg}^0$  oxidation was also identified on the commercial SCR catalyst employed in this study. The activity of  $\text{CuCl}_2/\text{TiO}_2$  catalysts for mercury oxidation was also very high over 80% of conversion and increased with the increase of  $\text{CuCl}_2$  loading and HCl concentration.  $\text{Hg}^0$  oxidation efficiency exceeding 90% was obtained over  $\text{CuCl}_2/\text{TiO}_2$  catalysts containing copper content of 3 wt% or more.

However, there was large difference in  $\text{Hg}^0$  oxidation efficiency between  $\text{CuCl}_2/\text{TiO}_2$  catalyst and commercial SCR catalyst in the absence of HCl. A commercial  $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$  SCR catalyst showed a very low activity less than 15% of  $\text{Hg}^0$  oxidation efficiency in the absence of HCl. On the other hand, more than 60% of elemental mercury was oxidized to oxidized mercury over  $\text{CuCl}_2/\text{TiO}_2$  catalysts and oxidation efficiency was increased with the amount of  $\text{CuCl}_2$  loading even in the absence of HCl. Practically, 100% of oxidation efficiency was obtained over  $\text{CuCl}_2/\text{TiO}_2$  catalysts containing copper content of 3 wt% or more even in the absence of HCl. This may suggest that mercury oxidation could occur by Cl released by the decomposition of  $\text{CuCl}_2$  on the catalyst. It was already identified that Cl was released by the decomposition of  $\text{CuCl}_2$  at higher temperature at which  $\text{Hg}^0$  oxidation could proceed, as observed by the elemental analyses and XRD measurement in Table 2 and Fig. 2. It may imply that Cl in  $\text{CuCl}_2$  on the catalyst surface act as oxidant to sustain  $\text{HgCl}_2$  formation even in the absence of gas phase HCl promoting mercury oxidation.





**Fig. 4.** Effect of HCl concentration on the oxidation of elemental mercury to oxidized mercury under SCR condition; gas flow rate = 2 L/min, reaction temperature = 350 °C, [NO] = [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 3%, [Hg] = 50 µg/m<sup>3</sup>, [HCl] = 0–50 ppm, [N<sub>2</sub>] balance.

The CuCl<sub>2</sub> on CuCl<sub>2</sub>/TiO<sub>2</sub> catalyst after decomposed was easily restored to its original form by gas phase HCl as identified by the elemental analyses and XRD measurement. Granite et al. [19] proposed that mercury oxidation could occur via a Mars–Maessen mechanism that adsorbed Hg<sup>0</sup> would react with a lattice oxidant such as O or Cl that is replenished from the gas phase. For CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalyst, the Mars–Maessen mechanism can be confirmed by the observation of mercury oxidation even in the absence of gas phase HCl. Therefore, the Mars–Maessen mechanism could be proposed for Hg<sup>0</sup> oxidation over CuCl<sub>2</sub>/TiO<sub>2</sub> catalyst on which adsorbed or weakly bound Hg<sup>0</sup> would react with Cl in CuCl<sub>2</sub> that is replenished from the gas phase HCl. This mechanism may be consistent with the observation of enhanced Hg<sup>0</sup> sorption to halogen-promoted sorbents and fly ashes [19,25].

### 3.3. Effect of HCl on the oxidation efficiency of Hg<sup>0</sup> under SCR condition

To examine the effect of reactant gas compositions on the activity of the same catalysts tested under oxidation condition, the activity of CuCl<sub>2</sub>/TiO<sub>2</sub> catalysts for Hg<sup>0</sup> oxidation under SCR condition was examined as shown in Fig. 4. Note that the reactant gas stream was composed of 3% O<sub>2</sub> in N<sub>2</sub> balance under oxidation condition, while NH<sub>3</sub> and NO were additionally contained in the reactant gas under SCR condition. Since the SCR reaction between NH<sub>3</sub> and NO could occur, it was named as SCR condition, when NH<sub>3</sub> and NO were present in the reactant gas stream. The activity of commercial SCR catalyst for Hg<sup>0</sup> oxidation was negligible in the absence of HCl, but significantly increased with the increase of HCl concentrations, indicating HCl is inevitably necessary component for mercury oxidation. However, the effect of HCl on the oxidation of Hg<sup>0</sup> to oxidized mercury was relatively low under SCR condition compared to that under oxidation condition. The maximum oxidation efficiency of commercial SCR catalyst obtained under SCR condition was about 63% at the reaction temperature of 350 °C and HCl concentration of 50 ppm in our experimental conditions. As discussed in the previous study, much lower activity of commercial SCR catalyst for mercury oxidation under SCR condition than under oxidation condition was attributed to NH<sub>3</sub> preventing the adsorption of HCl promoting the Hg<sup>0</sup> oxidation [35]. Note that NH<sub>3</sub> present in the reactant gas stream under SCR condition has been well known to easily and strongly adsorb on the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-based SCR catalyst surface [37,38]. NH<sub>3</sub> would preferentially adsorb on the catalyst surface when NH<sub>3</sub> and HCl were present simultaneously in the reactant gases. In our previous study, it was observed

that much less amount of Hg<sup>0</sup> was adsorbed on the commercial SCR catalyst surface under SCR condition than under oxidation condition, even in the absence of HCl [35]. This indicates NH<sub>3</sub> inhibits the adsorption of not only HCl but also Hg<sup>0</sup> on the catalyst surface under SCR condition. Therefore, there would be less available sites for the adsorption of HCl promoting the Hg<sup>0</sup> oxidation under SCR condition with NH<sub>3</sub>. In addition to our study, there have been consistent reports on the inhibition effect of NH<sub>3</sub> for Hg<sup>0</sup> oxidation [30–34,36].

CuCl<sub>2</sub>/TiO<sub>2</sub> catalysts showed much higher activity for Hg<sup>0</sup> oxidation than commercial SCR catalyst, and the activity increased with the increase of CuCl<sub>2</sub> loading and HCl concentration as shown in Fig. 4. Compared to that of commercial SCR catalyst, the enhancement of activity of CuCl<sub>2</sub>/TiO<sub>2</sub> catalyst for Hg<sup>0</sup> oxidation was much more apparent under SCR condition than under oxidation condition in the presence of HCl. CuCl<sub>2</sub>(3)-V<sub>2</sub>O<sub>5</sub>(2)/TiO<sub>2</sub> catalyst containing about 2 wt% of V<sub>2</sub>O<sub>5</sub> revealed higher activity than commercial SCR catalyst with similar V<sub>2</sub>O<sub>5</sub> content. This indicates that CuCl<sub>2</sub> on the catalyst surface plays an important role for Hg<sup>0</sup> oxidation. This may also indicate that the Hg<sup>0</sup> oxidation over CuCl<sub>2</sub>/TiO<sub>2</sub> catalyst occurs via a quite different mechanism than that over commercial SCR catalyst.

The activity of SCR catalyst was negligible less than 10% in the absence of HCl. Like the result obtained under oxidation condition, however, CuCl<sub>2</sub>/TiO<sub>2</sub> catalyst showed considerable activity for Hg<sup>0</sup> oxidation even in the absence of HCl under SCR condition as shown in Fig. 4. As discussed above, this indicates the Cl species in CuCl<sub>2</sub> act as chlorine source to oxidize elemental mercury to oxidized mercury. The apparent enhancement of Hg<sup>0</sup> oxidation by HCl under SCR condition and the observation of considerable Hg<sup>0</sup> oxidation even in the absence of HCl seem to be decisively proof of the involvement of Mars–Maessen mechanism over CuCl<sub>2</sub>/TiO<sub>2</sub> catalysts. This mechanism can explain the reason why CuCl<sub>2</sub>/TiO<sub>2</sub> catalyst shows much higher activity for mercury oxidation than commercial SCR catalyst under SCR condition containing NH<sub>3</sub> in the reactant gas stream which prevents the mercury oxidation by HCl.

The trace constituents such as CO, SO<sub>3</sub>, NO and SO<sub>2</sub> of actual flue gas have been known to impact the heterogeneous oxidation of mercury. It has been previously suggested that CO, NO and SO<sub>2</sub> can impact the heterogeneous oxidation of mercury by stripping adsorbed chlorine species from the surface of the catalyst with the formation of carbonyl chloride, nitrosyl chloride and sulfuryl chloride, respectively [20,21,23]. It has also been suggested that NO and SO<sub>2</sub> could have an impact on the oxidation of mercury by stripping adsorbed oxygen from the surface of the catalyst to form NO<sub>2</sub> and SO<sub>3</sub>, respectively [20,21,23]. Sulfur trioxide has been shown to inhibit the removal of mercury by activated carbons. It has been speculated that the oxidation of sulfur dioxide and sulfur trioxide to sulfuric acid can significantly impact the chemistry of mercury on the surface of sorbents and catalysts [20,21,23,43,44]. From the practical point of view, future work should be examined in more detail for the impacts of some of the trace constituents such as CO, SO<sub>3</sub>, NO and SO<sub>2</sub> of actual flue gas upon the oxidation of mercury over the present catalytic system. In particular, SO<sub>2</sub> can affect the structure of CuCl<sub>2</sub> acting as a vital component to promote Hg<sup>0</sup> oxidation in our catalytic system. A systematic study on the effect of SO<sub>2</sub> upon both of Hg<sup>0</sup> oxidation and NO removal activity of CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalyst is being prepared in our laboratories.

### 3.4. NO removal activities of CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalysts

Since this study was addressed to develop a catalyst for simultaneous removal of mercury and NO in SCR process, NO removal activities of CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalysts were also examined as shown in Fig. 5. NO removal activities of commercial SCR catalyst

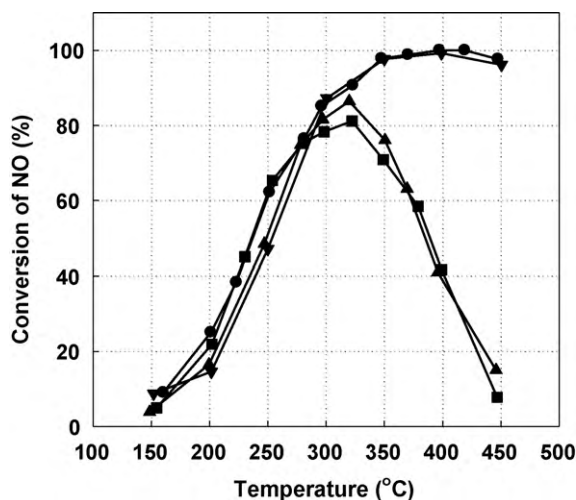


Fig. 5. NO conversion with respect to reaction temperatures; (■) CuCl<sub>2</sub>(3)/TiO<sub>2</sub>, (▲) CuCl<sub>2</sub>(3)-V<sub>2</sub>O<sub>5</sub>(2)/TiO<sub>2</sub>, (●) V<sub>2</sub>O<sub>5</sub>(2)/TiO<sub>2</sub>, (▼) commercial SCR catalyst. Reaction conditions; gas flow rate = 2 L/min, catalyst weight = 1 g, [NO] = [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 3%, [N<sub>2</sub>] balance.

(V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>) and home-made V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst were also included to compare with those of CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalysts. The activity of commercial SCR catalyst for NO removal was increased with the increase of reaction temperatures and showed maximum conversion of nearly 100% above the temperatures of about 350 °C. It showed wide operating temperature window from about 300 °C which is the temperature range operated optimally in actual SCR process. A V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst showed similar trend in NO conversion to that of commercial SCR catalyst with respect to reaction temperatures.

The catalysts containing CuCl<sub>2</sub> showed quite different behavior of NO removal activity with respect to reaction temperatures, compared to those of commercial SCR catalyst (V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>) and home-made V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst. NO conversions of CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalysts significantly decreased with the increase of reaction temperatures from about 320 °C. Therefore, CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalysts revealed a bell-shaped activity of NO conversion with the increase of reaction temperatures, which is a typical characteristic of SCR catalyst caused by NH<sub>3</sub> oxidation actively occurring at higher temperatures [27]. This suggests that copper species including CuCl<sub>2</sub> on the catalyst surface are intimately involved in the oxidation of NH<sub>3</sub> which is fed to reduce NO in SCR process. There have been many reports that copper species including CuCl<sub>2</sub> on the catalyst surface showed high activity for a variety of oxidation reactions [39,45–47]. Further systematic study seems to be needed to clarify the role of copper species on the surface of CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalyst for SCR reaction including NH<sub>3</sub> oxidation.

#### 4. Conclusions

The catalytic activities of CuCl<sub>2</sub>/TiO<sub>2</sub>-based catalysts with different loadings of CuCl<sub>2</sub> were examined to investigate the role of copper chloride for the oxidation of gaseous elemental mercury in SCR process. The main copper compound on the catalyst was identified as CuCl<sub>2</sub> by XRD measurement, indicating that CuCl<sub>2</sub> was well loaded on the catalyst surface by simple impregnation method employed in this study. Based on the elemental analyses and XRD measurement, it was found that CuCl<sub>2</sub> on CuCl<sub>2</sub>/TiO<sub>2</sub> catalyst was decomposed releasing Cl by calcinations at high temperatures and restored to its original form by being exposed to gas phase HCl, reversibly. The activity for mercury oxidation was significantly increased with the increase of CuCl<sub>2</sub> loading and HCl concentration. In particular, the enhancement of activity of CuCl<sub>2</sub>/TiO<sub>2</sub>-based

catalysts for Hg<sup>0</sup> was apparent than that of commercial SCR catalyst under SCR condition. The catalysts revealed high activity for mercury oxidation even in the absence of HCl. This indicates the Cl species in CuCl<sub>2</sub> act as chlorine source to oxidize elemental mercury to oxidized mercury. This suggests that mercury oxidation could occur via a Mars–Maessen mechanism by which adsorbed or weakly bound Hg<sup>0</sup> would react with Cl in CuCl<sub>2</sub> that is replenished from gas phase HCl. However, the activity of CuCl<sub>2</sub>-loaded catalysts for NO removal greatly decreased with the increase of temperature above 300–350 °C, which may be due to the ability of CuCl<sub>2</sub> for NH<sub>3</sub> oxidation in SCR reaction.

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